Microtopography of the barite (0 0 1) face during growth: AFM observations and PBC theory

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Abstract

Under moderate supersaturation conditions, crystal growth on the barite (0 0 1) surface takes place by the development of two-dimensional nucleation simultaneously with the advancement of molecular-height cleavage steps on the surface. The most frequent growth steps have a height of a half-unit cell, as has been predicted by periodic bond chain (PBC) theory, and they are parallel to the $\langle 1\,2\,0 \rangle$ PBC directions. Along opposite directions the velocity of $\langle 1\,2\,0 \rangle$ growth steps is strongly anisotropic. Moreover, the directions of fast growth alternate for successive elementary growth layers. The anisotropy of the growth rates can be explained by taking into account the crystallographic features and orientation of the complete PBC within each (0 0 2) elementary growth slice. On the other hand, the alternation of the fast growth direction for $\langle 1\,2\,0 \rangle$ steps in successive d_{002} growth layers is related to the existence of a 2_1 screw axis perpendicular to the (0 0 1) surface. Two-dimensional nucleation on the barite (0 0 1) surface is characterized by the development of islands with a circular sector shape and half-unit cell in height. The two-dimensional islands nucleated on the initial surface show the same orientation. As growth proceeds, islands coalesce and a homogeneous layer with a thickness of 3.5 Å is formed. Nucleation on this new surface produces islands oriented in the opposite sense to those in the previous layer. Goniometric measurements and X-ray diffraction experiments confirm that the straight edges of the islands are parallel to the [1 2 0] and [1 $\bar{2}$ 0] crystallographically equivalent directions. The third side of each island is curved, rough and tangent to [0 1 0]. Both the morphology and development of two-dimensional nuclei on the barite (0 0 1) face clearly indicate that the growth process is structurally controlled. The asymmetry of [1 2 0], [1 $\bar{2}$ 0] and [0 1 0] PBCs and their crystallographic features can be considered as responsible for the geometry and spread of the circular sector islands formed on each elementary (0 0 2) growth layer.

1. Introduction

In recent years atomic force microscopy (AFM) has been demonstrated to be an excellent technique for testing classical crystal growth models [1,2]. In situ AFM crystallization experiments in a fluid cell, under controlled conditions of temperature and supersaturation, allow the observation of growing crystalline surfaces at a molecular level. These detailed observations frequently indicate the existence of an interrelation between surface structure and

external conditions, such as the degree of supersaturation or fluid composition during the crystal growth process [3]. While external conditions and specific surface energies essentially control both nucleation kinetics and growth mechanisms, the surface structure of each $\{h\,k\,l\}$ growing face directly influences the specific microtopographic features (i.e. orientation and height of growth steps, two-dimensional (2D) nuclei shapes and their development, etc.).

In order to evaluate the structural control on crystal microtopography during growth, previous knowledge of the possible elementary growth layers and their crystallographic characteristics is required. It is well known that certain substances exhibit surface reconstruction or relaxation processes which can modify the growing layer structure. For the barite (0 0 1) face, however, the difference between relaxed and unrelaxed surface energies is quite small [4] and it can be assumed that relaxation is not important. Therefore, the atomic surface structure for the barite (0 0 1) face can be successfully derived from the bulk structure. For this purpose, PBC theory has been demonstrated to be a very useful tool [5]. On the basis of the distribution and strength of bonds within crystal structures the PBC method leads to the determination of the elementary growth layers for a given face [6,7]. On the other hand, the application of PBC analysis to actual crystal structures allows the prediction of possible growth steps and provides information about their relative stability [8].

In this paper we report AFM in situ observations of barite growth. Under the supersaturation conditions employed, the development of 2D nucleation and step advancement on the barite (0 0 1) surface occur simultaneously. According to Hartman and Heijnen [7] the elementary growth layers of the barite (0 0 1) face consist of uniquely defined F slices with thickness $\frac{1}{2}d_{0\,0\,1}$ (3.5 Å). Growth on the barite (0 0 1) face must occur, therefore, by half-unit cell slices alternating in space and time. Here, we present an experimental confirmation of the existence of such (0 0 2) slices during barite growth. Moreover, both the growth behaviour of monomolecular steps and the 2D morphology of the nuclei are interpreted in terms of the crystallographic features of the steps contained in the (0 0 2) elementary slice, as derived by PBC theory.

2. Experimental procedure

Barite crystal growth experiments have been carried out at 25°C in situ in a fluid cell of a Digital Instruments Multimode AFM, working in contact mode. The barite samples were optically clear single crystals freshly cleaved on (0 0 1). In order to be able to follow the complete growth process and to avoid excessive nucleation, all experiments were conducted using static solutions. $BaSO_4$ aqueous solutions were prepared by mixing Na_2SO_4 and $BaCl_2$ or $Ba(NO_3)_4$ solutions (SIGMA 99 + %). The concentrations of the $BaSO_4$ solutions employed ranged from 60 to 105 μM. Supersaturations were calculated by using the program SEA [9]. This program calculates the activities for the relevant chemical species present in the solution (Ba^{2+}, SO_4^{2-}, $NaSO_4^-$, HSO_4^-, OH^-, H^+, $BaOH^+$, $BaSO_4^0$ and $NaOH^0$) by employing the Debye–Hückel method. Once the activities of these species are known the supersaturation with respect to barite is obtained from the following expression

$$\beta = a(Ba^{2+})\,a(SO_4^{2-})/K_{sp}, \tag{1}$$

where $a(Ba^{2+})$ and $a(SO_4^{2-})$ are the activities of the free ions in the solution and K_{sp} is $10^{-9.96}$ at 25°C.

The orientation of the barite crystals was determined by X-ray diffraction in a Philips PW-1050 diffractometer using monochromated Cu K_α radiation data.

3. AFM observations

The supersaturations calculated using the Eq. (1) for the $BaSO_4$ solutions employed in this work ranged from $\beta = 26.7$ and 75.5 (corresponding to the concentrations 60 and 105 μM $BaSO_4$, respectively). For sparingly soluble substances, such is the case of barite, highly supersaturated solutions without inducing nucleation can be formed. The calculated β values can be considered, therefore, as moderate supersaturations.

For the range of concentration solutions employed, cleavage step advancement and 2D nucleation on the barite (0 0 1) face occur simultaneously [10]. For each type of crystal growth process, observations of the geometry and anisotropy of the growth were made.

3.1. Cleavage step growth

It is well known that freshly cleaved barite surfaces show different cleavage steps, whose orientation is related to the velocity of propagation of the cleavage front [11]. Among these possible steps, monomolecular height steps parallel to ⟨1 2 0⟩ directions are the most frequent ones. Under low and moderate supersaturations, cleavage steps can advance until they reach the edge of the face. Further growth on F face has to take place, however, by means of spiral steps generated on screw dislocations or by 2D nucleation. Fig. 1a shows an image of a typical barite (0 0 1) surface taken after flowing supersaturated $BaSO_4$ solution through the fluid cell for 10 s. In this image growth steps parallel to the [1 2 0] direction coexisting with a number of 2D nuclei can be observed. These ⟨1 2 0⟩ monolayer steps have a half-unit cell in height (3.5 Å) and exhibit a highly anisotropic displacement with the fastest growth direction alternating for successive elementary growth layers. Fig. 1a illustrates this behaviour of the growth steps aligned parallel to the [1 2 0] direction. This figure shows a number of ⟨1 2 0⟩ growth steps, each of height d_{002}. Observations of the growth of these steps normal to the [1 2 0] direction show that one-half layer grows faster in one of these perpendicular directions whereas the next half-unit cell layer grows faster in the other. In the schematic diagram of Fig. 1b, the crystallographic orientations of the steps and the slow and fast growth directions in successive layers are shown. The measured velocities of the [1 2 0] growth step along the fast directions ranges have a value of $\sim 0.2\ \mathrm{nm\ s^{-1}}$, while the velocity along the slow directions is practically negligible.

3.2. Two-dimensional nucleation

Fig. 1 also shows sector-shaped 2D nuclei on the (0 0 1) surface. These 'islands' form a few seconds

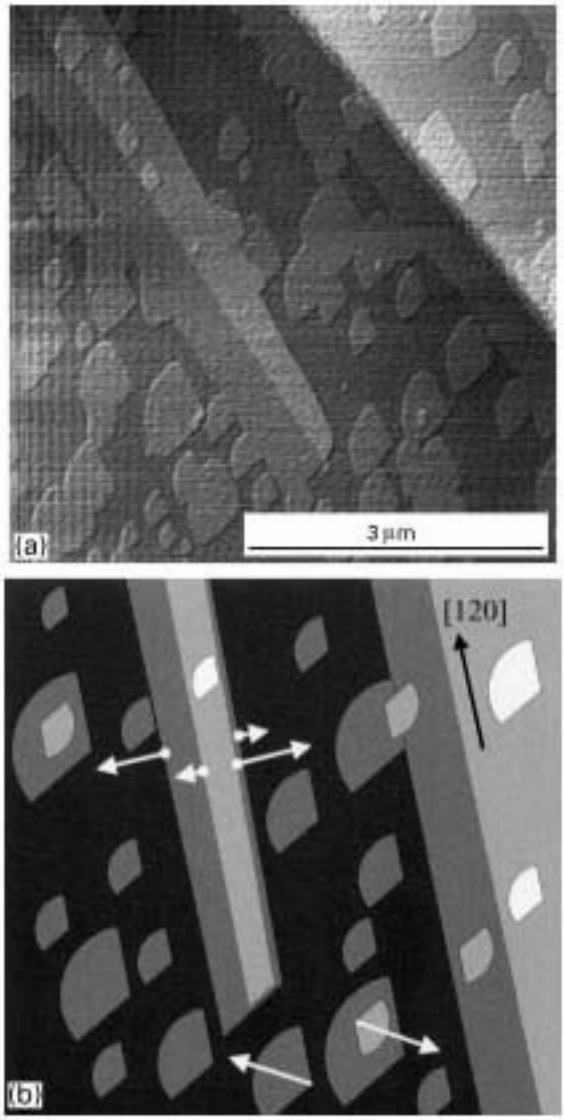


Fig. 1. (a) Growing barite (0 0 1) surface in supersaturated solution ($\beta = 75.5$). The image was taken in constant force mode while displaying the cantilever height signal (scan area: $6 \times 6\ \mu m^2$). Monomolecular steps parallel to the [1 2 0] direction and 2D nuclei coexist on the same surface. Both growth steps and 2D islands have a half-unit cell in height (3.5 Å). The advance of [1 2 0] steps is anisotropic and alternation of fast growth directions in successive growth layers can be observed. (b) Growth model for the advancement of [1 2 0] steps and 2D nucleation in successive growth layers. The short and long arrows indicate slow and fast growth directions, respectively.

after the injection of the $BaSO_4$ solution. They appear to be randomly distributed on the pre-existing surface with a nucleation density ranging from 4 to 300 nuclei/μm^2, depending on the initial supersaturation of the solution [10]. As in the case of growth steps, the surface nuclei are a half-unit cell (3.5 Å) in height. The islands have a characteristic circular sector shape with two straight sides forming an obtuse angle. Goniometric measurements indicate that the obtuse angle is always close to 101.7°, i.e. the angle formed between the crystallographically equivalent [1 2 0] and [1 $\bar{2}$ 0] directions. X-ray diffraction experiments confirm that these straight edges are parallel to the [1 2 0] and [1 $\bar{2}$ 0] directions. In contrast to these well-defined edges the third edge of the islands is curved and shows a rough boundary. Fig. 2a shows a barite (0 0 1) surface partially covered by small islands with their characteristic morphology. All the islands deposited on the same surface have the same orientation.

The nucleation of barite surface islands and their subsequent growth support the 'birth and spread' model proposed by Ohara and Reid [12]. The way in which the nuclei spread indicates that [1 2 0], [1 $\bar{2}$ 0] and [1 0 0] directions are the faster growth directions. Under the initial supersaturation conditions employed here, the values for the growth rate of the islands, obtained by measuring their length along [1 0 0] at different times, are similar to that observed for the fast directions of $\langle 1\,2\,0 \rangle$ growth steps.

As growth proceeds, neighbouring islands come into contact and coalesce, eventually forming a homogeneous layer with a thickness of 3.5 Å. However, before a complete growth layer is formed on the original cleavage surface a new 2D nucleation event occurs on this freshly-grown surface. The nucleation density on the new layer is similar to that measured on the initial surface, but the most obvious difference is that these new islands are oriented oppositely with respect to those on the layer below (Fig. 2b). Fig. 3 shows a schematic 3D representation of the arrangement of the circular sector islands grown on two successive elementary growth layers. Both the orientation of the islands and their morphology are consistent with barite (0 0 1) symmetry. Islands have a mirror plane which

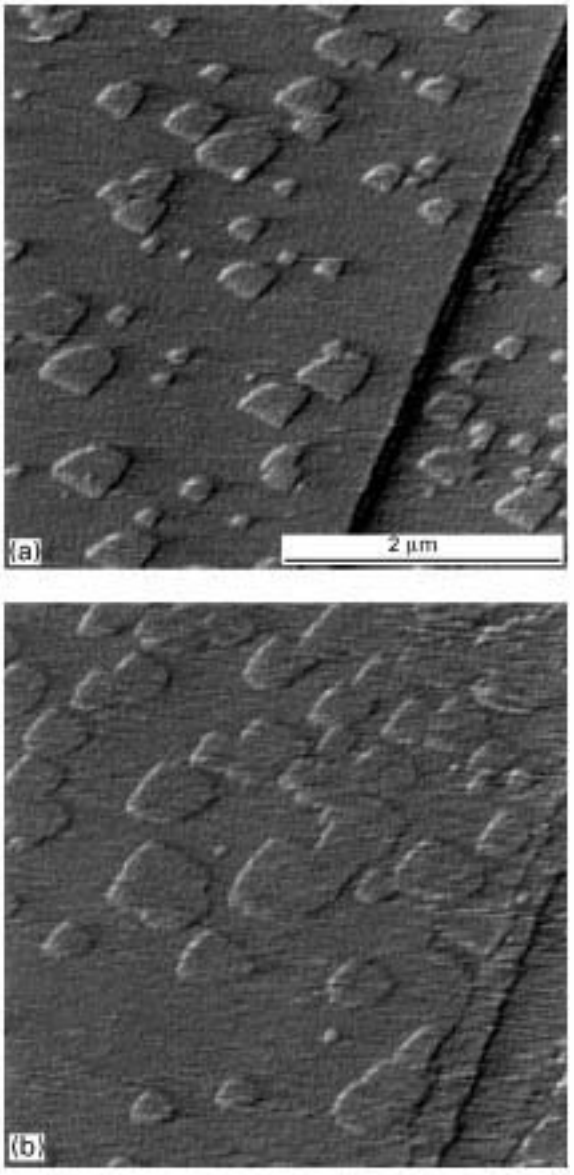


Fig. 2. Growing barite (0 0 1) surface in supersaturated solution ($\beta = 26.7$). The images were taken in constant force mode while displaying the deflection signal (scan area: 4 × 4 μm^2). (a) About 10 s after injecting the supersaturated solution, a number of 2D nuclei with circular sector shape is formed. The islands are oriented pointing in the same direction. (b) The same area as (a) 17.12 s later. A second 2D nucleation event on the new layer formed by the coalescence of the previous islands consists of the deposition of islands which are oriented oppositely with respect to the former one.

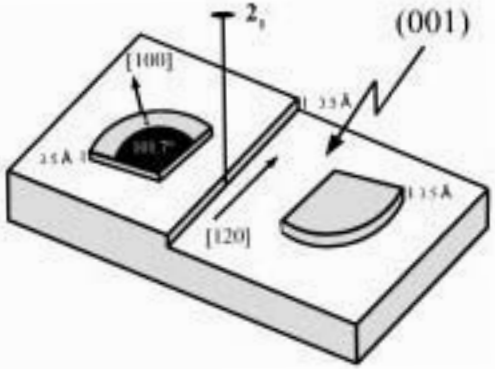


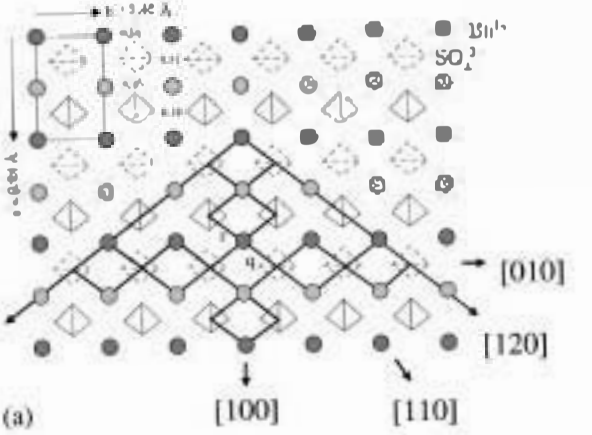
Fig. 3. Schematic 3D representation showing the barite circular nucleus islands formed in successive (0 0 2) elementary growth layers. The main crystallographic and geometrical features are indicated.

is parallel to the (0 1 0) mirror plane in the barite structure. The two opposite orientations of the surface islands grown in successive elementary growth layers are related by the 2_1 screw axis parallel to c.

4. Discussion

The geometrical features of the growth steps observed on the barite (0 0 1) surface as well as the orientation of the 2D nuclei and their development during growth clearly indicate that the surface crystallography strongly controls the nucleation and growth process. The anisotropic advancement of growth steps on the (0 0 1) face, and the growth behaviour of the barite islands can be justified on the basis of the orientation and crystallographic characteristics of the periodic bond chains (PBCs) contained in the successive (0 0 2) elementary growth slices.

Barite ($BaSO_4$) crystallizes in the orthorhombic space group Pnma with lattice parameters $a = 8.884$ Å, $b = 5.458$ Å and $c = 7.153$ Å [13]. According to Hartman and Heijnen [7] the elementary growth layers for the barite (0 0 1) have a half-unit cell height and they are uniquely defined. These (0 0 2) slices have a strong F character and contain PBCs along [1 0 0], [0 1 0], ⟨1 1 0⟩ and ⟨1 2 0⟩ directions. Fig. 4a and Fig. 4b shows two projections of the barite structure down [0 0 1] showing



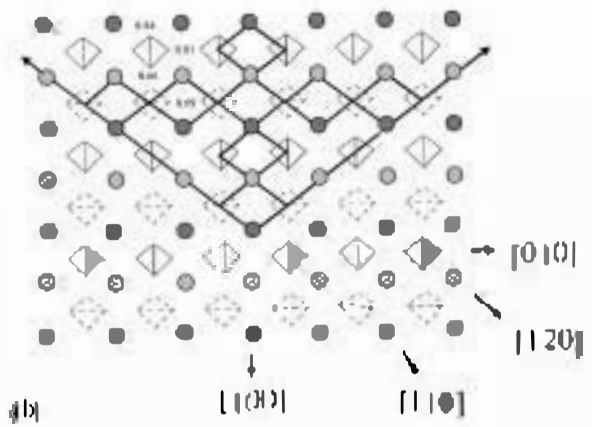


Fig. 4. (a) The structure of one barite (0 0 2) elementary growth layer projected along [0 0 1] direction. The heights of both the S atoms in the SO_4^{2-} tetrahedra and the Ba^{2+} cations are indicated. In this projection the [1 0 0], [0 1 0] and ⟨1 2 0⟩ PBCs within the structure have been drawn. For the sake of simplicity the (1 1 0) PBCs have not been marked. The PBCs consist of a combination of bonds parallel to [1 0 0] and ⟨1 2 0⟩ directions. Although all the PBCs contained within the (0 0 2) slice are formed by similar sequences of q and r bonds they exhibit a different degree of sinuosity. (b) Similar projection of the next (0 0 2) growth layer showing the changed orientation of the PBCs.

the differences between the two successive (0 0 2) growth layers. The PBC vectors lying within each (0 0 2) layers consist of sequences of two different Ba–SO_4 bonds (q and r) with similar bond energies (1568 kJ/mol for q and 1547 kJ/mol for r) [6]. PBCs along ⟨1 2 0⟩ and [1 0 0] directions are formed by the bond sequence q–r–q–r with chain

repeating periods of 14.07 and 8.88 Å, respectively. A similar sequence can be also found running parallel to the [1 1 0] direction, with an identity period of 10.43 Å. Finally, the bond sequence for the PBCs parallel to the [0 1 0] direction is q–q or r–r, with a translational period of 5.45 Å. Although the PBCs within (0 0 2) slice layers are built up from a similar sequence of bonds with about the same bond energy, they differ in geometry and hence in the atomic configuration of the incorporation sites (i.e. kink sites) along them. There is experimental evidence to support the idea that, when the growth proceeds by monomolecular steps, the kink structure plays an important role [14]. Differences in kink concentration or kink integration energies will strongly determine the kinetics of step growth.

Step advancement during barite (0 0 1) face growth occurs perpendicularly to the PBCs which run parallel to the steps. Due to this fact, differences in the bonding geometry of kink sites at both sides of complete PBCs will determine differences in the ionic polarization, dehydration energies and, therefore, in the motion of steps advancing along opposite senses. Inspection of the PBCs contained within each elementary (0 0 2) growth layer shows that, except for the [1 0 0] PBC, which is parallel to a mirror plane, all the PBCs within this slice are asymmetric. As a result, kink sites are not equivalent at both sides of steps parallel to those PBCs and an anisotropic motion for most of the monomolecular steps on barite (0 0 2) growth layer can be expected. This is in agreement with the displacement observed for the ⟨1 2 0⟩ steps, which exhibit a measurable motion along one sense while along the opposite one the growth is negligible. Only for the [1 0 0] steps, whose kink sites at both sides of the corresponding PBC are related by symmetry, an isotropic spreading rate for the opposite [0 1 0] and [0 $\bar{1}$ 0] directions can be expected, although this has not been observed because [1 0 0] steps rarely occur on freshly cleaved (0 0 1) surfaces.

The shape, orientation and development of the 2D nuclei can also be related to the PBCs on the (0 0 1) barite surface. Circular sector islands of thickness 3.5 Å contain four PBCs: [0 1 0], [1 0 0], [1 2 0] and [1 $\bar{2}$ 0]. Among these PBCs, [1 2 0], [1 $\bar{2}$ 0] and [0 1 0] basically define the island shape: straight edges of surface nuclei are parallel to the symmetrically equivalent [1 2 0] and [1 $\bar{2}$ 0] PBC vectors, while the curved and microscopically rough third side is tangent to the direction [0 1 0]. The fourth non-equivalent PBC parallel to [1 0 0] PBC lies between these two directions (see Fig. 2a and Fig. 2b).

The morphological inequivalence of the island boundaries indicates differences between the growth behaviour of the steps. Inspection of the structure projection shown in Fig. 2a and Fig. 2b reveals that PBCs parallel to the ⟨1 2 0⟩ steps are made up of a straight sequence of bonds and a relatively low number of kink sites along them are displayed. As a result, island edges parallel to ⟨1 2 0⟩ directions will be straight and well defined. Conversely, [0 1 0] PBCs, are formed by undulating chains of Ba–SO_4 bonds with a high kink site density. Therefore, [0 1 0] steps are structurally rough, the incorporation of growth units along them is favoured and an irregular spread can be expected.

Finally, it seems clear that once an island nucleates on a barite (0 0 1) surface its further growth is strongly controlled by the asymmetry of the [1 2 0], [1 $\bar{2}$ 0] and [0 1 0] PBCs. As we mentioned previously, for growth steps parallel to asymmetric PBCs, which displays different kink site bond geometry at both sides (see Fig. 4a), an anisotropic advancement can be expected. In the case of steps on barite (0 0 2) elementary growth layers, this anisotropy is extreme (i.e. the step advancement perpendicularly to their corresponding PBC direction is only measurable along one of the two senses) and a limited number of growth directions are possible. Due to this fact, the spread of the initial 2D nuclei is constrained to the directions lying between [1 2 0] and [1 $\bar{2}$ 0]. These directions, and the intermediate direction [1 0 0], represent fast growth directions corresponding to PBCs based on analogous bond sequences. Both the attachment of growth units along them and the lateral migration of the steps at the crystallization front, which is favoured by the high number of kink sites displayed along the [0 1 0] PBC, can be considered responsible for the development of the characteristic rounded side of the 2D islands. On the other hand, the similar growth velocities observed for [1 2 0], [1 $\bar{2}$ 0] and [1 0 0] directions explain why the islands

retain their circular sector shape during the growth process.

The explanation given above for both the motion of the growth steps and the development of barite islands is valid for successive growth layers if we consider that (0 0 2) elementary growth slices are related by a 2_1 screw axis. This symmetrical constraint implies a change in the orientation of the PBCs of one slice with respect to the next one and, therefore, it leads to the rotation of kink sites. As a result, an alternation, during growth, of the fast advancement directions for ⟨1 2 0⟩ cleavage steps occurs. For the case of the 2D nucleation the alternation of incorporation kink sites during growth will be reflected in the alternate orientation of barite islands on successive growth layers.

5. Conclusions

The in situ AFM observations of the barite (0 0 1) face during growth reveal that, under moderate supersaturation conditions, advancement of ⟨1 2 0⟩ steps and the development of circular sector-shaped 2D nuclei occur simultaneously. The growth steps, as well as the 2D nuclei, have a half-unit cell height (3.5 Å), which is the thickness of the elementary growth layer predicted by PBC theory. Both the anisotropy of the displacement of ⟨1 2 0⟩ growth steps and the morphology of the 2D islands indicate a clear crystallographic control of the overall growth process. On the one hand, the behaviour of the ⟨1 2 0⟩ growth steps can be justified taking into account the different bonding geometry of kink sites at both sides of the ⟨1 2 0⟩ PBCs, which will determine differences in the ionic polarization, dehydration energies and, therefore, in the motion of steps advancing along opposite orientations. On the other, and the asymmetry of the [1 2 0], [1 $\bar{2}$ 0] and [0 1 0] PBCs and differences in the kink site density, can be considered as directly responsible for the characteristic morphology and development of the circular sector islands. Finally, both the alternation of fast growth directions of the ⟨1 2 0⟩ steps and the opposite orientation of the 2D islands in successive growth layers can be interpreted as a consequence of the existence of a 2_1 screw axis parallel to *c*.

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